Assistance Agreement Quarterly Report: 5th Quarter

Date of Report: March 14, 2001

Agreement No: R82806301

Title: **Baltimore Supersite: Highly Time and Size Resolved Concentrations of Urban PM2.5 and its Constituents for Resolution of Sources and Immune Responses**

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Research Category: Particulate Matter Supersites Program

Project Period: January 15, 2000 to December 31, 2003

Objectives of Research: Our primary objectives are to i) provide an extended, ultra high-quality multivariate data set, with unprecedented temporal resolution, designed to take maximum advantage of advanced new factor analysis and state-of-the-art multivariate statistical techniques; ii) provide important information on the potential for health effects of particles from specific sources and generic types of sources, iii) provide large quantities of well characterized urban PM for retrospective chemical, physical, biologic analyses and toxicological testing, iv) provide sorely needed data on the sources and nature of organic aerosol presently unavailable for the region, v) provide support to existing exposure and epidemiologic studies to achieve enhanced evaluation of health outcome-pollutant and -source relationships, and vi) test the specific hypothesis listed in our proposal.

Readiness

We are working hard to complete preparations to begin the 1-month Baltimore Supersite Intensive sampling period scheduled to begin on or about May 1st. We believe that delays in delivery of some items (notably mass spectrometer vacuum pump) may delay startup, but are optimistic that any delay will be less

than 2 weeks. Our most distressing problem is that, at this time MDE will not have FRM Mass and speciation samplers available for the May intensive campaign, nor will they have gas monitors available. We are hoping to solve this problem.

Progress Summary/Accomplishments

LIDAR. Additional preliminary measurements were made with the JHU three-wavelength LIDAR from the Homewood campus. The laser was returned to the manufacturer for repair and delivery is expected by the end of March. JHU has successfully made mixing height calculations from the data. The group has designed and provided a preliminary data output files, including numerical data and image files for mixing height and relative particle concentration data.

SEAS. A new SEAS system has been constructed employing newly designed glass components, new connectors (ball joints and other gasket seal type joints), new low volume Teflon valves, new perflurocarbon peristaltic pump tubing, the addition of thermostatic control of the steam generator, and a new plexiglass support frame. Several replacement parts for each of the glassware components have been built. The new virtual impactors have been checked and ground to achieve uniform nozzle diameters and appropriate pressure drops. We have developed cleaning protocols for each component, including all glassware, o-rings, and valves. The new system has been assembled and is being "blanked." System blanks are now up to 10-fold lower than the previous version of the instrument. Several bulk slurry samples have been collected (with the prior version of the system) for analytical and cytokine assay testing. These have been analyzed by GFAA and by ICPMS, with good agreement for most elements. Results of replicate analyses after as much as 50 days of storage show that most metals are stable in solution without freezing. Exceptions are Al and Fe, which we believe to be on settleable particles or in unstable colloidal suspensions. Al and Fe may require stabilization by appropriate additives. We are preparing to investigate these. We expect the system to be operational on time for our May 1 intensive. We are awaiting delivery of the new fraction collectors for the SEAS chemistry and SEAS cytokine systems.

Single Particle MS. We have refined the format for acquiring the single particle MS data and import function for the project database. All of the long lead time items have arrived except for the power supplied and turbo pump. A new turbo pump configuration has been designed and ordered. It consists of two split turbo pumps along with one extra stage on the inlet. This will enable one less pump to be used while decreasing the gas load to the source region. The reduced gas load will keep the machine cleaner and lower the background been completed. We are hopeful that the pumps will arrive in time to begin the field study on May 1.

Cytokine Assays. Five milliliters of a SEAS bulk sample, i.e., a volume which should represent a typical 1-hr sampling period, were divided into 4 aliquots of successively larger (doubling) volume and the aliquots tested in the IL-8 cytokine assay. A highly linear dose-response curve was obtained. The results suggest that we will be able to successfully measure cytokine responses in the SEAS slurry samples to be collected in the Baltimore Supersite Project. Results of additional assay work, undertaken to determine assay reproducibility are being compiled.

Sulfate Monitor. After careful consideration, we have selected the R&P continuous sulfate monitor for

use in the project. The instrument has been ordered and delivery is expected by the end of March.

Organic Compound Sampler. We submitted a purchase order to Tisch Enviornmental for the construction of major components of our custom designed organic filter/PUF sampler. The sampler is designed to permit sequential sampling for up to 4 periods at flowrates up to 500 LPM and simultaneous collection of a 24-hr sample at 100 LPM. A Marple PM2.5 virtual impactor inlet has been cleaned and Teflon coated, a series of Teflon solenoid valves have been received, Teflon ball valves have been ordered, a valve timing circuit has been designed and is being built at the University of Maryland's electronics shop, and timer components have been ordered. We expect to take delivery on all components by the end of the first week in April.

UltraHigh-Volume Aerosol Sampler. A new control program for the system has been developed. The stainless steel 1-m cyclone has been removed and an all-aluminum cyclone has been temporarily installed for pressure drop, flow, and efficiency testing. Pending results of the tests, the cyclone will be Teflon coated and permanently installed. Or a slightly smaller cyclone will be constructed and installed. The unit is to be operational for use at Clifton Park beginning June 30.

QAPP/SOPs. During this quarter, we submitted the draft Quality Assurance Project Plan (QAPP) for review. The review has recently been returned to us from the EPA. Appropriate revisions have been made and the revised document was resubmitted. We anticipate final approval of the QAPP well before field work commences in May. We have written a first draft of the Data Management SOP and expect to have it available for review by the end of March. Professor Hopke has been actively participating in the weekly data manager's conference calls to define the format for distribution of the project data to NARSTO in fulfillment of the terms and conditions of the Supersite Cooperative agreement.

Data base development. We have begun basic data base design and are developing output file formats for all instruments to be operated at the Baltimore Supersite. Test files are being generated for use in developing import functions for the data base. The delivery of the data storage computer has been delayed because of the recall of the large 1" height SCA drives. To circumvent this problem, a new enclosure, i.e., one which will accept standard half-height drives which are available, was specified and ordered. We now expect delivery on our data storage machine by March 24. The machine will initially have a RAID 5 array of five 72 GB drives and will have capacity ofr another five 72 GB (or larger) hard drives, permitting a storage capacity of up to 510 GB (total capacity is reduced because of redundancy requirements for RAID 5 configurations). We intend to store all of the supersite raw data, including all QA/QC and diagnostic data from the instruments, with the possible exceptions of LIDAR and Single Particle MS data.

Website: Our Static Web site (www.chem.umd.edu/supersite) contains color maps of the Baltimore Region have been prepared in ARCVIEW and loaded onto our website. The maps show major PM emission sources (obtained from the EPA AIRS data base), metals emission sources (TRI data), and estimates of emissions as well as the location of our sampling sites and key streets. Recently, we've added a site plan for the supersite at Clifton Park; our position papers on the RH issue and allocation of intensive resources; the efficiency curve for the UMCP all glass inlet impactor; SEAS data taken at College Park, MD, showing resolution of sources; and a 2-D scan showing relative particle concentration data showing traffic pollution over Baltimore streets. Current versions of all SOPs are now available on the web site.

Site Permission and Preparation. Allied Trailer company has started construction of our two laboratory trailers. Delivery is scheduled for April 1st. The chain fence at the Clifton Park site has been enlarged to accommodate the 5 laboratory trailers that will be located there. Arrangements have been made to power the supersite trailers at the FMC site. A telephone and two ISDN lines have been ordered for the Clifton Park site.

Coordination with MDE and neighboring states. We have had several communications with MDE about the Clifton Park site; i.e., power and site layout of trailers. In addition we have been in contact with Ted Erdman (Region III Chief) and Michael Zuvich (Pennsylvania Dept. of Environmental Protection) to discuss the allocation and scheduling of speciation samplers and what measurements these will provide. Ted Erdman has indicated that Speciation Measurements will encompass the following: PM mass and elements by XRF on Teflon filters; ions (sulfate, total nitrate, ammonium, sodium, and potassium) by ion chromatography on Nylon filters; and EC/OC and carbon species as determined via thermal-optical analysis of quartz filters.

Previously, Drs. Ondov and Tuch met with several Maryland MDE representatives and Rolf Zeisler from NIST to discuss resource allocations and power requirements at the Clifton Park Supersite. Victor Guide from EPA Region III also attended. Pending written authorization from Region III, MDE agreed to move their PAMS site to Clifton Park for the duration of the Supersite Project. PAMS meausrements include VOC canister collections during the ozone season, as well as semicontinuous chromatographic VOC measurments. MDE agreed to provide the requested FRM, Speciation, and continuous mass monitoring equipment. These systems will be operated on a 1 in 3 day basis (every day during intensive sampling campaigns) by UMCP and MDE personnel. Subsequently, Ted Erdman has provided authorization by email for the purchase of two sets of speciation samplers, analysis of samples, and purchase of a continuous PM2.5 monitor. However, at this time, MDE support will apparently be unavailable until June 30.

Personnel Changes. Dr. Yu-Chen Chang joined the UMCP Supersite Team on January 16th, 2001. Doctoral student, Dawn Catino, joined our group on February 10th. Ms. Catino's work will encompass RDI/sychrotron XRF measurements.

Publications/Presentations/meetings:

No publications have yet been prepared. Dr. Ondov visited Professor Thomas Cahill's laboratory at UC Davis and also visited the Berkeley Synchrotron XRF facility during the week of December 4th, 2000. The purpose was to assess applicability to the Baltimore Supersite Project and obtain information needed for the QAPP and analytical SOP. Dr. Ondov visited Professor Philip Hopke to investigate applications of factor analysis models to SEAS data already collected at College Park, MD. We have invited our advisory committee members to visit the Baltimore supersite during the last week in May. We will attend the EPA supersite PI s meeting at RTP on March 20th and 21st.

Future Activities:

1. We will continue to hold weekly PI teleconferences as needed
2. Additional Instruments to be purchased include: Drum impactors (we are working with Dr. Thomas Cahill on this).
3. Additional SEAS samples will be collected and delivered to UMAB for cytokine assay testing.
4. Assay testing will continue to determine appropriateness and reproducibility.
5. Tests of the Filter/PUF sampler are scheduled to be completed in April.
6. The data management SOP is scheduled to be completed by the end of April.
7. The data storage computer is scheduled to be installed on March 24th.
8. The initial components of the project relational data base are to be installed by April 15th.
9. Methods to stabilize Al and Fe in SEAS slurry samples will be developed.
10. The Baltimore Supersite project will initiate its 12-month field study on or about 1 May, 2001.

Supplemental Keywords: Single Particle Mass Spectrometry, ROS, Cytokine, Receptor Modeling

APPENDIX A: PROJECT CHANGES

1. Intensive campaigns

Primary purpose:	i) gather source profiles, ii) support JHU exposure/epi studies
Original Proposal:	two (winter/summer) 45-day intensives at urban industrial site
Revised Proposal:	one 30-day intensive at urban industrial site; two 30-day intensives at urban supersite
Reasons:	Dubious advantage to winter campaign at industrial Allows for short-term Filter/PUF, 8-stage RTI, and daily FRM sampling at urban site; Continues to Support JHU exposure/Epi studies Moving intensive up to May gives i) benefit of source profile information in selecting samples for retrospective analyses and Need move equipment only once Allows for intensives at urban supersite (Clifton Park) for comparison/coordination with other Eastern SSs in July intensive

2. Organic Sampling Strategy

Original Proposal:	Five 24-hr samples/month @ 113 LPM, separate Filter/PUF analyses Consecutive 1 to 2 hr samples/@ 500 LPM; retrospectively analyze 90 separate Filter/PUF samples. Collect/analyze a few denuder/Filter/PUF samples; Analyze a few Bulk PM2.5 samples
Purpose:	Explore nature of organic compounds present Provide data for source attribution (We originally intended to obtain annual mean concentrations)
Problem:	Original Proposal provides too few samples to effectively use advanced statistical analyses. It provides data for transition periods (non winter and non summer months) but these are not judged to be terribly useful.
Revised Proposal:	Five consecutive 24-hr samples @113 LPM for two months (i.e., during intensives), extract and analyze Filter/PUF samples together. Collect consecutive 3-hr samples @500 LPM during 2 intensives. Analyze 104 combined Filter/PUF samples (13 days worth per

intensive + blanks.
Collect/analyze denuder/Filter/PUF and Bulk PM samples as specified above.

3. SEAS

Decline to field GFAAZ at sites. Little advantage. Creates QC/QA inconsistency between near-real time and retrospective analyses, Can process more samples for complete suite of elements at UMCP lab., allows better support of Pittsburgh and St. Louis Supesites. Could consider fielding GFAAZ near end of field project.

Inlet size cut: We are considering PM1.2 inlet. RE: removal of coarse dust component for improving source resolution and improved analytical efficiency. Have sharp-cut glass 1.2 :m cyclone available. Final decision will be made after the new SPMS inlet is calibrated and tested.